Identification and quantification of methyl halide sources in a lowland tropical rainforest

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Cite as:
Blei, E., Hardacre, C.J., Mills, G.P., Heal, K.V. and Heal, M.R. (2010) Identification and quantification of methyl halide sources in a lowland tropical rainforest, *Atmospheric Environment* ***44***, 1005-1010. doi:10.1016/j.atmosenv.2009.12.023

Abstract

In conjunction with the OP3 campaign in Danum Valley, Malaysian Borneo, flux measurements of methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) were performed from both tropical plant branches and leaf litter in June and July 2008. Live plants were mainly from the *Dipterocarpaceae* family whilst leaf litter samples were representative mixtures of different plant species. Environmental parameters, including photosynthetically active radiation, total solar radiation and air temperature, were also recorded. The dominant factor determining magnitude of methyl halide fluxes from living plants was plant species, with specimens of the genus *Shorea* showing persistent high emissions of both gases, e.g. *Shorea pilosa*: 65±17 ng CH_3Cl h^{-1} g^{-1} (dry weight foliage) and 2.7±0.6 ng CH_3Br h^{-1} g^{-1} (dry weight foliage). Mean CH_3Cl and CH_3Br emissions across 18 species of plant were 19 (range, <LOD – 76) and 0.4 (<LOD – 2.9) ng h^{-1} g^{-1} respectively; fluxes from leaf litter were 1 to 2 orders of magnitude smaller per dry mass. CH_3Cl and CH_3Br fluxes were weakly correlated. Overall, the findings suggest that tropical rainforests make an important contribution to global terrestrial emissions of CH_3Cl, but less so for CH_3Br.

Keywords:

CH_3Br, CH_3Cl, dipterocarp, emission, rainforest, South-East Asia, stratospheric ozone.

Introduction

Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl), two naturally-occurring trace gases in the atmosphere, are estimated to contribute up to 25% of present-day ozone destruction by halogens in the stratosphere (WMO, 2007). The relative importance of these two gases will

increase as implementation of the Montreal Protocol takes effect, making them an important factor in the chemistry of future climates. However, the global budgets of CH_3Cl and CH_3Br remain quite uncertain, with a significant shortfall in estimated sources for both gases (Butler, 2000; WMO, 2007).

Observations during airborne (Gebhardt *et al.*, 2008) and shipborne (Yokouchi *et al.*, 2000) campaigns, together with modelling studies (Lee-Taylor *et al.*, 1998; Yoshida *et al.*, 2006), suggest that there are unaccounted for tropical terrestrial sources of these methyl halides. The *Dipterocarpaceae* (dipterocarps) have recently been identified as one plant family with species that emit significant amounts of CH_3Cl (Yokouchi et al., 2002; Saito et al., 2008). These are pantropical arboreal plants making up a substantial part of the rainforest in South East Asia as well as growing in both the African and South American tropical regions (Ashton and Appanah, 2004). Another possible methyl halide source of global importance is leaf litter (Lee-Taylor and Holland, 2000; Drewer *et al.*, 2008), but this has not been evaluated by in situ measurements in the tropics. Laboratory studies have also demonstrated senescent plant material as a temperature-dependent source of methyl halides (Hamilton *et al.*, 2003; Wishkerman *et al.*, 2008).

There are almost no data for CH_3Cl fluxes, and none for CH_3Br fluxes, from living plants, or leaf litter, in situ in tropical rainforest. This provided the motivation for this field study, carried out in June and July 2008 in the Danum Valley Conservation Area, near Lahad Datu, Malaysian Borneo, in parallel with the OP3 campaign (Oxidant and Particle Photochemical Processes above a South East Asian tropical rain forest) (Hewitt et al., 2009). Static chamber techniques were used to make the first measurements of fluxes of CH_3Cl and CH_3Br for a number of dipterocarp and other tropical plant species as well as for leaf litter. Possible drivers of these fluxes were investigated.

Experimental

Flux measurements were made on branches of trees and seedlings at the Danum Valley Field Station (4°58′ N, 117°48′ E, 400 m a.s.l.) and at the Innoprise-FACE Foundation Rainforest Rehabilitation Project (INFAPRO) nursery nearby, c.70 km inland. The ecosystem in this area is the largest remaining pristine lowland dipterocarp forest in the Malaysian state of Sabah. In total, 48 measurements were carried out in June and July 2008 on 18 different species comprising replicate measurements on the same individuals as well as on different individuals of the same species (Table 1). Thirteen of the species investigated were from the *Dipterocarpaceae* family, but *Crateva religiosa* (*Capparaceae*), *Etlingera brevilabrum* and *Etlingera elatior* (*Zingiberaceae*), *Syzygium campanulatum* (*Myrtaceae*) and *Eusideroxylon zwageri* (*Lauraceae*) were also included. The height of sampled branches ranged between 1.5 and 2.5 m above the ground. Measurements were undertaken during both day and night.

Branches were enclosed in transparent chambers of either 26 L (polycarbonate) or 66 L (polyethylene terephthalate) volume, equipped with forced air circulation. Seedlings were enclosed in a 66 L chamber. During the 20 min enclosure period, internal and external air temperature, photosynthetically-active radiation (PAR) and total solar radiation were recorded with data loggers. In this work, time of day and solar flux were not directly correlated since the trees were standing in a valley, subject to shading by hillside or other trees according to the angle of the sun. At the end of the enclosure time a 550 mL air sample was extracted and stored in a 1 L Tedlar bag. Contemporaneous samples of ambient air were collected and stored similarly. At the end of each sampling period, the total number of leaves on the enclosed branch was counted and a subset of the foliage removed and its dry weight determined by oven drying at 70°C until constant weight.

Leaf litter was collected from seven representative 10 m^2 plots within the rainforest surrounding the Danum Valley Field Centre. Each collection area comprised leaf litter from a variety of plant species. Triplicate sub-samples of between 250 and 450 g fresh leaf litter from each location were enclosed (on site) for 24 h in opaque 12 L containers after which a 550 mL air sample was withdrawn and stored in a 1 L Tedlar bag. Two data loggers recorded ambient temperature at 1.5 m height, and within an adjacent enclosed empty container, whose air was also sampled as a blank. Leaf litter dry weight was determined as above.

Gas samples were analysed for CH_3Br and CH_3Cl either at Danum Valley on the University of East Anglia GC-MS or couriered to the University of Edinburgh for analysis. In the latter case, all samples were analysed within two weeks of collection.

On-site analysis used an online pre-concentrator (UNITY and Online Air Server; Markes International Ltd., Llantrisant, UK) coupled to an Agilent 6890 gas chromatograph with a MS5973N mass spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA) operating in either electron impact (EI) or negative ion chemical ionization (NICI) mode and single ion monitoring mode (Worton *et al.*, 2008). A 500 mL aliquot of each sample was pre-concentrated onto a mixed Carbograph 1 TD/Carboxen 1000 trap cooled to -10°C with a two-stage Peltier cell. The trap was then heated to 250°C to transfer the analytes in high purity helium carrier gas (99.9999%) onto the RTX-502.2 column, length 105 m, i.d. 0.32 mm (Restek, Bellefonte, PA, USA). The temperature programme was 30°C for 2 min, heat at 8°C min^{-1} to 150°C, hold for 16 min, heat at 20°C min^{-1} to 220°C, and hold for 5 min. NICI was most commonly used, with a limit of detection (LOD) for CH_3Cl of ~30-60 pptV. However, some samples were analysed using EI, with an LOD for CH_3Cl of 0.3 pptV. Accuracy and precision were ±6% and ±3%,

respectively, for CH_3Cl determination at 45 pptV by NICI or 5 pptV by EI. Calibrations were performed every 8 samples by analysing 500 mL of a gas standard containing atmospheric levels of analytes calibrated against the gravimetric primary gas standards for CH_3Cl and CH_3Br on the 'NOAA 2003' scale (www.esrl.noaa.gov/gmd/hats/standard/scales.html).

In Edinburgh, 100 mL aliquots of each sample were analysed using an HP5890 GC-ECD with a custom-built two-stage cryogenic pre-concentration unit (Hardacre *et al.*, 2009). The first stage comprised an absorbent trap filled with Tenax TA 60/80 (Supelco, Bellefont, PA, USA), cooled with two-stage Peltier cells to -28°C. The second stage was a cryogenic trap filled with glass beads and cooled with dry ice to -78°C. Separation was carried out with a ZB642 column (Phenomenex Inc., Torrence, CA, USA), length 30 m, i.d. 0.32 mm, and a temperature programme of 5 min at 40°C, ramp to 240°C over 5 min and hold for another 5 min. Five-point calibrations were undertaken using dilutions into zero air from certified CH_3Br standard (500 ± 10 ppbV in N_2, Air Products Inc., Allentown, PA, USA), and CH_3Cl standard (15.80 ± 0.47 ppmV in N_2, Air Liquide, Paris, France). Accuracy and precision uncertainty combined was quantified as ±15% for both gases at mixing ratios around ambient.

Net fluxes were derived from the difference between sample and ambient background values (for branches) or blank container values (for leaf litter) and expressed per gram of dried material. The uncertainties in flux values quoted here combine the uncertainties in both instrumental determination of methyl halide concentration in a gas sample and in the enclosure parameters used to convert concentrations to flux. The main sources of uncertainty derive from interpolation of the calibration curve and, in the case of branch measurements, from scale up to total dry weight of leaf material enclosed. Blank and storage experiments were conducted and found not to contribute uncertainty greater than the general magnitude of the other uncertainties present and quantified. Since both the parallel background air and enclosure samples were

stored in identical conditions such uncertainties are minimised by the experimental design of quantification by difference. Discrimination of a significant net flux depends on the ability to determine significant difference in analyte mixing ratio between an enclosure sample and parallel background air sample. The LOD for determination of a net flux was thus set at twice the uncertainty in the associated background sample. The LOD values vary between individual flux measurements because the uncertainties in individual sample and background gas analyses, and in estimation of enclosed volume and foliage mass, vary between measurements (see also caption of Table 1).

Results and Discussion

A summary of all the flux measurements from individual tropical species is presented in Table 1. The magnitude of the fluxes was highly species dependent. Whilst some plants showed no emissions, the genus *Shorea* showed consistently high fluxes. CH_3Cl emissions from *Shorea agamii*, *Shorea macrophyla*, *Shorea pilosa* and *Shorea superba* were consistently large (flux > 10 ng h^{-1} g^{-1}) over several measurements, whilst *Shorea johorensis* and *Crateva religiosa* also had large CH_3Cl emissions in single measurements. The *Dipterocarpus applanatus*, *Dryobalanops lanceolata* and *Syzygium campanulatum* species were moderate CH_3Cl emitters (10 ng h^{-1} g^{-1} > flux > LOD). CH_3Br emissions were large (flux > 1 ng h^{-1} g^{-1}) for *Shorea pilosa* and *Crateva religiosa*, whilst *Dipterocarpus applanatus*, *Dryobalanops lanceolata*, *Eusideroxylon zwageri*, *Shorea agamii*, *Shorea falciferoides*, *Shorea macrophyla*, *Shorea superba* and *Syzygium campanulatum* were moderate CH_3Br emitters (1 ng h^{-1} g^{-1} > flux > LOD). Mean CH_3Cl and CH_3Br fluxes across the 18 species of plant investigated were 19 (range, <LOD – 76) and 0.4 (<LOD – 2.9) ng h^{-1} g^{-1} (dry weight foliage), respectively. Although the linear correlation was not strong, if plants were emitters of one methyl halide they were emitters of the other (Figure 1a, $R = 0.42$, $P < 0.004$).

Methyl halide fluxes from five *Dipterocarpaceae* species - *Dipterocarpus applanatus*, *Dryobalanops lanceolata*, *Hopea nervosa*, *Shorea agamii* and *Shorea pilosa* - were measured at intervals during the day and once during the night (Figure 2). There was evidence of a pattern for largest emissions during mid to late afternoon and continuing, but declining, emissions during the night, particularly for the two strongest emitters, *Shorea agamii* and *Shorea pilosa*. In some instances there was no apparent significant diurnal cycle. For these 5 species, there were no significant correlations between methyl halide fluxes and the measured environmental parameters of PAR, total solar radiation, air temperature and internal chamber temperature (although the datasets are comparatively small). Instead, the factor influencing emissions is species.

The data presented here are the first reported measurements of methyl halide emissions from live specimens of a number of important South East Asian tropical rainforest species, and the first such CH_3Br fluxes from any dipterocarp species. There is coherence with the findings of Saito et al. (2008), from a different part of South East Asia, that the *Dipterocarpacaeae* family is, in general, a strong emitter of CH_3Cl, but that fluxes vary widely between species. Saito et al. (2008) quantified CH_3Cl fluxes from small masses of excised leaves from 117 plant species, including 29 species of the *Dipterocarpaceae* family, following enclosure in 40 mL vials for 4-8 days. Of the 24 species with CH_3Cl emissions greater than 10 ng g^{-1} h^{-1}, 19 were dipterocarps with a median CH_3Cl emission rate of 30 ng g^{-1} h^{-1}. Here, a total of 41 measurements on 13 species of dipterocarps were carried out with mean emission rates of 30 ng g^{-1} h^{-1} for CH_3Cl and 0.55 ng g^{-1} h^{-1} for CH_3Br. There is therefore good correspondence between the two studies for CH_3Cl. The large emission of CH_3Cl from *Crateva religiosa* measured in this work is also consistent with the observation by Yokouchi et al. (2007) that this species was a strong CH_3Cl emitter, although the flux measured here was somewhat smaller than previously reported.

Analysis of the Cl^- and Br^- content of the plant material enclosed was not possible on site and export of plant material is restricted. Watling and Harper (1998) measured Cl^- in wood of 48 tropical species but none were species whose CH_3Cl fluxes were measured in our work, although their measurements did include a few other *Shorea* species whose Cl^- contents were 24, 39, 39, 69 and 187 mg kg^{-1} dwt wood. The range in the Watling and Harper (1998) Cl^- measurements spans more than two orders of magnitude (9 to 1014 mg kg^{-1}) and this range excludes two palm species (as not relevant to our study) with even higher Cl^- content. Overall, the mean Cl^- content for the 46 tropical species was 90 mg kg^{-1}, suggesting that the Cl^- contents of the wood of the measured *Shorea* species were not unusual. Lobert et al. (1999) provide a summary of Cl^- content in tropical (and temperate) wood, foliage and litter separately, again with a large range in individual measurements. Two general trends can be noted: (a) Cl^- content in foliage is higher, on average, than in wood, with litter concentrations intermediate between the two, for both temperate and tropical species; (b) Cl^- content in wood/foliage/litter of tropical species is higher, on average, than in temperate species. Data on Br^- content of plant species are more sparse. Lee-Taylor and Holland (2000) provide summary Br^- content of 3.7 mg kg^{-1} for tropical coarse wood detritus and 16 mg kg^{-1} for fine wood matter (assumed to include leaf litter) which are values circa one order magnitude lower than the Cl^- concentrations quoted above. As with Cl^-, Lee-Taylor and Holland (2000) also report that Br^- content in tropical forest material is, on average, higher than for temperate forest material. Data on variability of halogen content between different parts of the same individual or between individuals either in the same location or elsewhere are essentially non-existent.

There is certainly insufficient evidence at present to implicate a link, if any, between CH_3X flux and halogen content for dipterocarp species in particular, although the general observation of higher halogen content in plant material from the tropics is consistent with the greater

importance to CH_3X emissions generally ascribed to tropical rather than to temperate forests. However, it is known that many vascular plants contain a halogenating methyl transferase enzyme, and that CH_3X emission represents only a small proportion of the halogen content (Manley, 2002), so it seems likely that variation in expression of this enzyme in particular species and individuals will drive variation in CH_3X flux at least as much as intrinsic variation of tissue halogen concentration.

Any attempt at scaling up these plant-scale measurements to tropical rainforests globally is necessarily indicative, order-of-magnitude only. Assuming the leaf biomass per unit area of 900 g m^{-2} presented by Saito et al. (2008) for lowland tropical forest in Peninsular Malaysia is reasonable for similar forest in Malaysian Borneo, then applying the mean CH_3Cl and CH_3Br fluxes of 19 and 0.38 ng h^{-1} g^{-1} across all measured species in this work gives estimates for average canopy basal area CH_3Cl and CH_3Br fluxes of ~17 and ~0.34 μg m^{-2} h^{-1}, respectively. Multiplying by an area of 10.4×10^{12} m^2 for tropical evergreen rainforest globally (Guenther et al., 1995) yields global annual emissions of 1.5 Tg CH_3Cl and 30 Gg CH_3Br. These are probably overestimates since dipterocarp species were deliberately targeted in this work. According to Davies et al. (2003), cited in Saito et al. (2008), dipterocarps comprise ~30% basal area coverage in Malaysian rainforest. Applying a weighting of average emissions from dipterocarp and non-dipterocarp species separately yields estimated basal area CH_3Cl and CH_3Br fluxes of ~12 and ~0.2 μg m^{-2} h^{-1}, or annual global emissions of 1.1 Tg and 18 Gg, respectively. These latter values correspond to 25% and 9% of current estimated total global annual fluxes of ~4.4 Tg and ~200 Gg for CH_3Cl and CH_3Br, respectively, summarised by WMO (2007).

For leaf litter measurements there was generally good agreement in fluxes between the triplicate samples of leaf litter from each sampling location but large differences (up to 4 orders of

magnitude for CH_3Cl and 3 orders of magnitude for CH_3Br) between the different locations (Table 2). This could be due to different moisture regimes and microbiological activity of the leaf litter at each plot. Samples at each location were collected on different days and variation in antecedent rainfall caused substantial variation of water in the litter layer on the forest floor. The lack of significant correlation observed here between CH_3Cl and CH_3Br fluxes and water content in bulk field samples of leaf litter (R^2 = 0.18 and 0.19, respectively) contrasts with laboratory work on senescent leaves in which fluxes of CH_3Cl and CH_3Br were negatively correlated with water content (Hamilton *et al.*, 2003; Wishkerman *et al.*, 2008). A likely explanation for this discrepancy is the different nature of the leaf material used. Hamilton et al. and Wishkerman et al. used intact leaf material that was collected either before the onset or in a very early stage of decay in which the activity of fungi and bacteria was probably negligible. The leaf litter used in this work included substantial decomposing material and leaf-rotting microorganisms are known producers of CH_3Cl and CH_3Br (Harper, 1985; Moore *et al.*, 2005). Thus production could be the result of abiotic or micro-biotic activity or both. Despite the wide variation in the flux magnitudes, the significant correlation between CH_3Cl and CH_3Br fluxes for individual leaf litter samples (Figure 1b, R = 0.75, $P < 0.001$) suggests common processes pertaining to both gases.

Values for negative fluxes are only semi-quantitative since methyl halide uptake is limited by the initial amount of methyl halide inside the enclosure rather than by the rate of uptake by the leaf litter. Previously reported CH_3Br fluxes from leaf litter in temperate forests have been considerably higher with a mean flux of 4.3×10^{-2} ng g^{-1} h^{-1} for deciduous litter and 8.0×10^{-2} ng g^{-1} h^{-1} for needle litter (Drewer *et al.*, 2008) compared to an average flux of 1.4×10^{-3} ng g^{-1} h^{-1} in this study. Taking the mean and range of the flux values derived in this study and assuming a total area of 10.4×10^{12} m^2 for tropical evergreen rainforest globally (Guenther et

al., 1995) and a fine litter pool of 1537 g dry litter material per m^2 (Matthews, 1997) yields global annual flux values of 320 (-5.2 – 1900) Gg for CH_3Cl and 0.2 (-0.05 – 1.7) Gg for CH_3Br. This compares with the range in estimated global CH_3Cl production from tropical leaf litter of 30 – 2500 Gg y^{-1} derived from the Hamilton et al. (2003) laboratory study. The point estimates from this work correspond to ~7% and ~0.1%, respectively, of the overall global annual fluxes of CH_3Cl and CH_3Br, respectively (WMO, 2007); i.e. tropical leaf litter is likely an important source of CH_3Cl globally, but not of CH_3Br.

In conclusion, this work confirms the few recent field measurements indicating tropical rainforests are an important global source of CH_3Cl, both via direct emissions from living plants - from species of the dipterocarp family in particular - but also via decomposing litter on the forest floor. The point estimate here of ~1.4 Tg y^{-1} for global tropical rainforest CH_3Cl emission from both sources together is similar to the 1.3 Tg y^{-1} estimated from above-canopy concentration gradient measurements in Peninsular Malaysia (Saito et al., 2008) and the 1.5 ± 0.6 Tg y^{-1} estimated from airborne measurements in South America (Gebhardt et al., 2008). The significance of tropical rainforest to CH_3Br budgets globally is less clear. The mass ratio of average CH_3Br and average CH_3Cl emissions from the plant species investigated here was ~0.02 which is somewhat smaller than the 0.05 mass ratio in the currently-estimated global annual fluxes of the two gases (WMO, 2007). This, and the much lower leaf litter CH_3Br fluxes, imply tropical forests make less contribution to global CH_3Br emissions, a few % compared with a few 10s% contribution for CH_3Cl. However it is important to remember that raw data remain very sparse and global scale up highly simplistic. Uncertainty of emissions at the plant scale is dominated by the very large variation between species, rather than by external environmental parameters, which considerably hampers establishing quantitative connection between branch scale and above-canopy regional-scale measurements. Nevertheless it is clear that the extensive

change in tropical rainforest area instigated by humankind (Sterling and Ducharne, 2008) will continue to alter global fluxes of these gases.

Acknowledgements

EB and CJH gratefully acknowledge the University of Edinburgh and EastChem, respectively, for studentship funding. We thank the Carnegie Trust for the Universities of Scotland, and the University of Edinburgh Development Trust and Elizabeth Sinclair Fund, for their financial contributions to the fieldwork. We also acknowledge the support of the whole OP3 team, the State of Malaysia for permission to work in Sabah, and Bernadus Bala Ola for his invaluable help in plant identification.

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Table 1: Summary of methyl halide net fluxes from living trees in Danum Valley and INFAPRO nursery. The sd values combine analytical and concentration-to-flux conversion uncertainties, plus, for instances where replicate measurements were undertaken, the variation between measurements for a single species. Individual flux determinations have their own LOD value; the interquartile ranges of LOD values for the measurements shown in this table were 1.6-5.3 and 0.053-0.091 ng g^{-1} h^{-1} for CH_3Cl and CH_3Br fluxes, respectively.

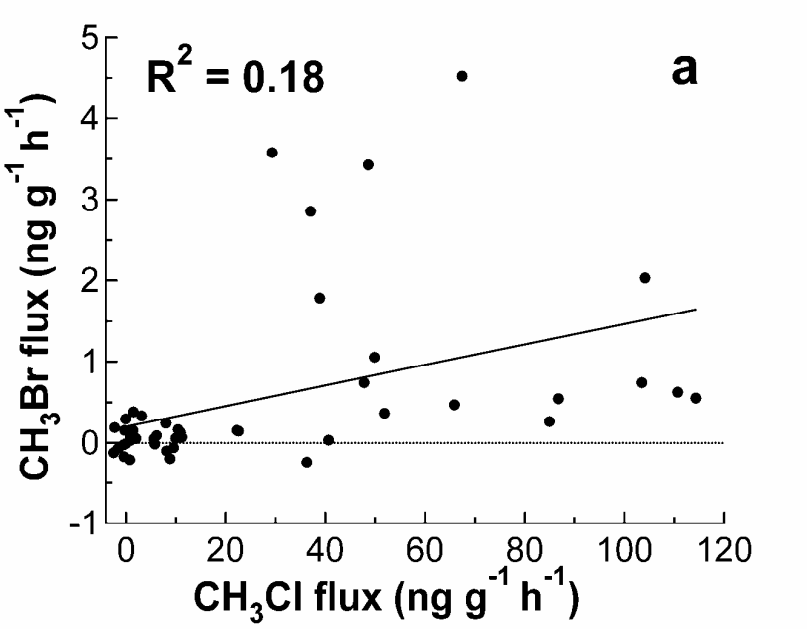
Species	no. of measurements [a]	CH_3Cl flux / ng g^{-1} dry wt h^{-1}				CH_3Br flux / ng g^{-1} dry wt h^{-1}			
		mean	sd	min	max	mean	sd	min	max
Crateva religiosa	1	37.1	7.9			2.86	0.53		
Dipterocarpus applanatus	5+1	8.4	4.2	< LOD	11.2	0.10	0.08	-0.10	0.30
Dipterocarpus confertus	1	< LOD	-			< LOD	-		
Dipterocarpus gracilis	1	< LOD	-			-0.025	0.018		
Dryobalanops keithii	1	< LOD	-			< LOD	-		
Dryobalanops lanceolata	4+1+1	4.8	3.1	< LOD	9.5	0.14	0.09	-0.06	0.38
Etlingera brevilabrum	2	4.2	5.7	< LOD	8.8	-0.18	0.08	-0.20	-0.17
Etlingera elatior	1	-	-			-0.08	0.05		
Eusideroxylon zwageri	1	< LOD	-			0.16	0.05		
Hopea nervosa	4+1+1	1.6	4.3	< LOD	5.6	0.04	0.11	-0.21	0.33
Parashorea malaanonan	1	-2.5	0.6			-0.12	0.05		
Shorea agamii	6+1	71.4	19.3	40.7	114	0.52	0.18	< LOD	1.05
Shorea falciferoides	1	< LOD	-			0.15	0.06		
Shorea johorensis (seedling)	1	36.3	7.9			-0.24	0.15		
Shorea macrophyla	2	76.3	15.1	65.9	86.7	0.51	0.10	0.47	0.54
Shorea pilosa	6	65.3	16.7	29.3	104	2.68	0.65	0.74	4.52
Shorea superba	2	22.4	3.7	22.2	22.6	0.15	0.06	0.15	0.16
Syzygium campanulatum	2	1.7	0.6	1.4	2.0	0.10	0.06	0.05	0.15

[a] for example, "5+1" indicates 5 measurements on one individual of the species plus one measurement on a second individual of the species.

Table 2: Mean CH_3Cl and CH_3Br fluxes for leaf litter from different parts of the rainforest. The sd values combine sampling and analytical uncertainties plus triplicate variation.

Sample plot	CH_3Cl flux / ng g^{-1} dry wt h^{-1}		CH_3Br flux / ng g^{-1} dry wt h^{-1}		% (w/w) water content
	Mean	sd	Mean	sd	
A	-2.4×10^{-3}	3.4×10^{-3}	-1.2×10^{-4}	1.6×10^{-4}	71
B	-5.2×10^{-3}	2.6×10^{-3}	-3.2×10^{-4}	0.7×10^{-4}	57
C	-6.0×10^{-3}	1.7×10^{-3}	-1.3×10^{-4}	0.3×10^{-4}	49
D	-3.9×10^{-3}	1.3×10^{-3}	-5.0×10^{-5}	3.1×10^{-5}	61
E	0.19	0.04	1.4×10^{-4}	0.5×10^{-4}	59
F	11	3.0	4.0×10^{-3}	1.1×10^{-3}	68
G	3.9	3.6	5.8×10^{-3}	3.5×10^{-3}	65

Figure 1: Correlations between CH_3Br and CH_3Cl fluxes from (a) individual live plant measurements, (b) individual leaf litter measurements. Note that negative fluxes (net uptake) for litter are only semi-quantitative.



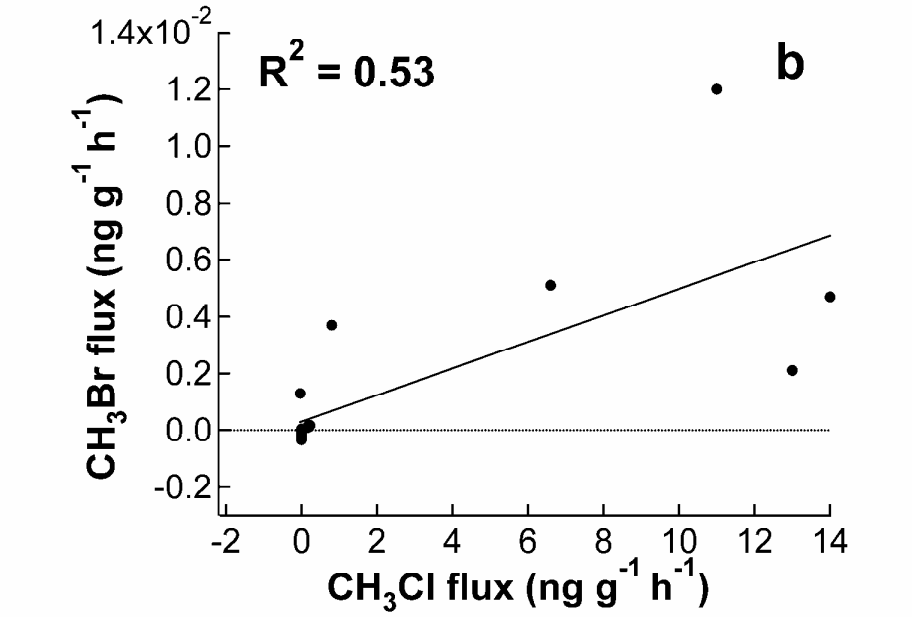


Figure 2: Diurnal CH_3Cl and CH_3Br fluxes from five different Dipterocarp species at Danum Valley: (a) and (c) *Shorea agamii* (—○—) and *Shorea pilosa* (···▲···); (b) and (d) *Hopea nervosa* (–■–), *Dipterocarpus applanatus* (—◇–) and *Dryobalanops lanceolata* (–×–). Whiskers incorporate both analytical and sampling uncertainties. Shaded areas mark hours between sunset and sunrise.